AUBE '01

12TH INTERNATIONAL CONFERENCE ON AUTOMATIC FIRE DETECTION

March 25 - 28, 2001
National Institute Of Standards and Technology
Gaithersburg, Maryland U.S.A.

PROCEEDINGS

Editors: Kellie Beall, William Grosshandler and Heinz Luck

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

M. Harms, J. Goschnick
Institute for Instrumental Analysis, Karlsruhe Research Center GmbH,
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen,
Germany, Phone +49-7247-822580, Fax +49-7247-824606,
Email: michael.harms@ifia.fzk.de

R. C. Young
National Aeronautics and Space Administration, Kennedy Space Center, Florida 32899, USA

Early Detection and Distinction of Fire Gases with a Gas Sensor Microarray

1. Introduction

The necessity of gas-analytical instruments for fire detection has been discussed in the past and is widely accepted at present. Conventional fire detectors usually work on a poor information basis, incapable of identifying the nature of the fire. Therefore, false alarms are often set off as gas concentrations, smoke densities or a high air temperature are mal-interpreted. This leads to the fact that many people do not consider fire alarm systems as reliable. Moreover, false alarms cause high costs due to the security measures triggered. For these reasons much faster and more reliable detectors are needed that are based on an additional discrimination power able to distinguish between the different occasions of gas release, but on the other hand incur no more costs than a conventional instrument.

The measurement of the electrical conductivity of semi-conducting metal oxides represents one way of realizing cheap and sensitive detection of gaseous components. Provided an array of metal oxide gas sensors is used, a high discrimination power in gas analysis can be realized. Using this principle, a novel type of gas sensor microarray based on the segmentation of a monolithic metal oxide layer by a set of parallel electrodes, has been developed at the FORSCHUNGSZENTRUM KARLSRUHE, that allows a sensitive detection and discrimination of gases at a very low cost.

2. Detection Principle

The principle of conductivity measurement at n-semi-conducting metal oxide fields for detection of gaseous atmospheric components has been well-known for about 40 years [1]. If a metal oxide surface is held at a temperature of some hundred degrees Celsius, adsorption and catalytic reactions of nearly all types of gases take place at the surface (see Fig. 1). The release of electrons by catalytic reactions (e.g. the oxidation of adsorbed hydrocarbons) or immobilization of conduction band electrons by adsorptive species, cause a gas specific change of the electrical conductivity of the metal oxide surface if the ambient gas composition is changed. If oxidizable gases such as methane are adsorbed on the surface, catalytic oxidation takes place, with electrons released to the conductivity band. As a result of adsorption and dissociation of gaseous oxygen molecules, negative oxygen ions are consumed during oxidation. Therefore, their level is kept low in the presence of air containing hydrocarbons or other oxidizable gases. However, if the latter disappear from the ambient atmosphere of the model oxide surface, the level of adsorbed oxygen ions rises to saturation, causing the conductivity to drop accordingly. By different mechanisms, not only oxidizable gases can be detected, but reducible ones as well – such as NO_2 and O_2 - or less active gases - as CO_2 [2]. Nearly all gases are detectable except for rare gases and other extremely passive gases, such as nitrogen.

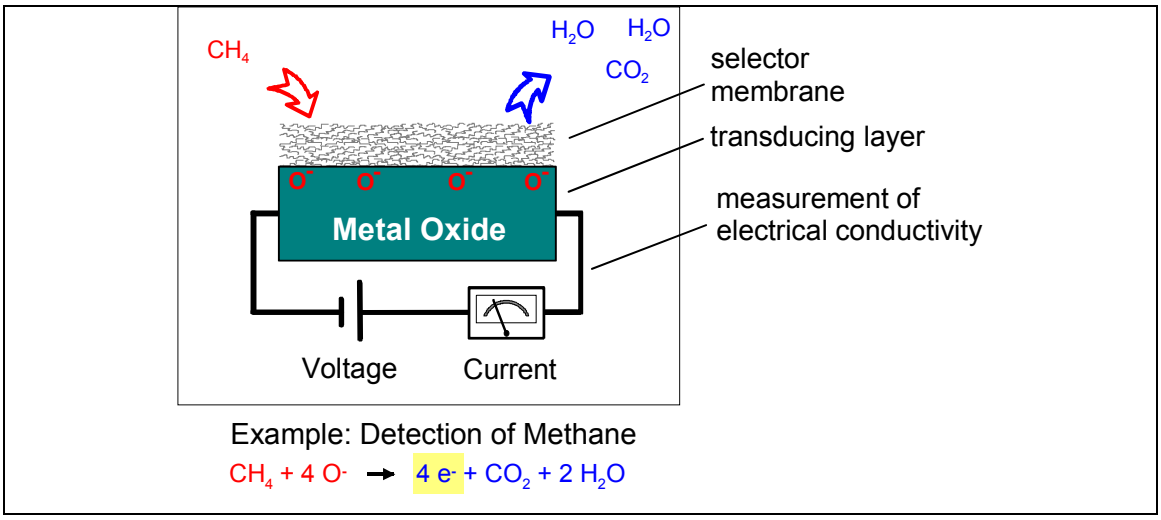


Fig. 1: Gas detection principle of metal oxide conductivity sensors. The detection of methane is shown as an example.

3. Gas Sensor Microarray

The great diversity of detectable gases can turn out to be a disadvantage for a single sensor if high selectivity for a particular atmospheric component is required. A sensor system with the ability to differentiate between gases can be set up if a multitude of different sensors is combined. Provided the sensitivity spectrum of each sensor, the so-called selectivity, is different from the other sensors of the array, exposures of the array to gases or gas ensembles result in a conductivity pattern, characteristic of the type and quantity of the gases contained in the gas mixture. The technological novelty of the microarray invented at the FORSCHUNGSZENTRUM KARLSRUHE, however, is the arrangement and differentiation between the gas sensors. Contrary to conventional macroarrays and other gas sensor microsystems, a single monolithic metal oxide film alone forms the basis of the whole array. This film is separated into 38 sensor segments by parallel electrode strips to measure the electrical conductivity of the individual segments [3]. The necessary operation temperature (usually between 200°C and 400°C) is provided by four meandering heating elements, placed at the reverse side of the chip (see Fig. 2). The heating power is controlled by two platinum thermoresistors, placed on the upper side of the chip. The whole array is coated with a permeable SiO_2 layer of variable thickness across the 38 sensor segments.

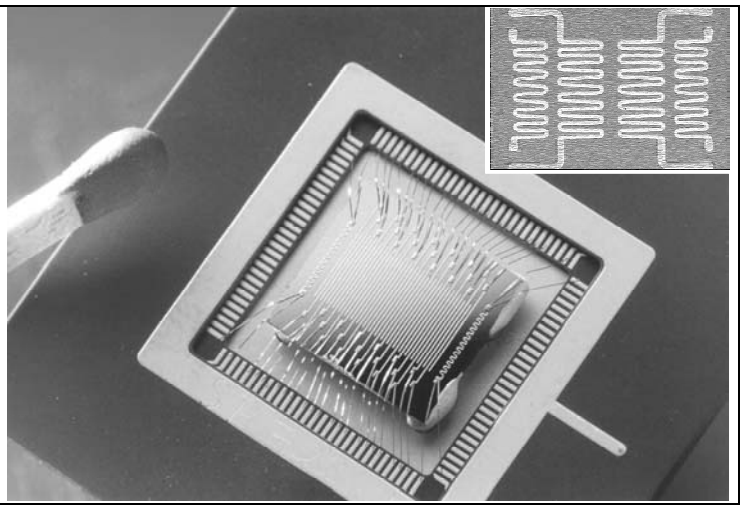


Fig. 2: Gas sensor microarray mounted in its housing. The front side consistis of the metal oxide detector field, separated into 38 sensor elements by 39 electrode strips. The reverse side carries four separate heating elements (on the upper right side).

4. Gradient Technique

The gradient technique serves to differentiate gas detection selectivity via the 38 individual sensor segments. The thickness of the ultra-thin gas-permeable SiO_2 membrane

layer deposited on top of the metal oxide film varies across the array (s. Fig. 3). Additionally, a controlled temperature gradient, e.g. of 50 K, is maintained across the array. Depending on the nature of the gases, due to diffusion through the membrane and the warmth caused by gas reactions at the metal oxide interface, gas detection selectivity is gradually modified from sensor segment to sensor segment. Therefore, the exposure to single gases or gas ensembles (like odors) cause characteristic conductivity patterns at this gradient microarray. The dependence of the conductivity pattern on the type and quantity of ambient gases allows gas discrimination and quantification.

Hence, this gradient microarray can be applied to realize an electronic nose system at a low cost: the Karlsruhe Micro Nose (KAMINA). Micro-fabrication is uncomplicated and thus inexpensive, especially thanks to the simple but high level integration of the sensor elements into the gradient array structure. Further functional advantages are reliability, stability and sensitivity of the gas-analytical performance.

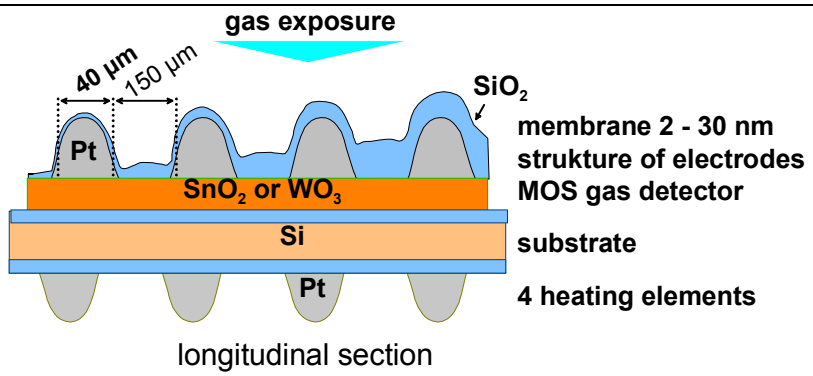


Fig. 3: Longitudinal section of the microarray. A SiO_2-membrane of a few nanometer. Thickness covers the metal oxide layer including the electrode structure. The thickness of the membrane varies across the sensor array in order to differentiate between the selectivity of the individual sensor segments.

5. Experimental

In the first stage of the fire detection study, two different kinds of microarrays were tested using defined concentrations of fire relevant gases. Representing typical components of fire gases, benzene, formaldehyde, tetrafluoro methane, hydrogen cyanide, and carbon monoxide were chosen as test gases. Two types of microarray chips were used in order to determine the most appropriate one for this kind of application: one was

coated with tin dioxide doped by 1 % platinum (SP chip) and the other with tungsten trioxide (WO chip). Furthermore, the best operation temperature for the microarray was determined. In this stage, gas concentrations in the range of 1 – 100 ppm were used. The concentrations were set by a computer-controlled mixing system, producing defined pulses of test gases alternating with clean air at a r. h. of 60 %. The signal response to the test exposures was used to determine the analytical performance of the microarray chips including sensitivity, detection limits, and response times. The gas concentrations were checked by applying conventional analytical methods (e.g. PID, FTIR). The experiments were repeated four weeks later using the selected chip with its optimal operation temperature in order to determine long time stability. Gas concentrations in the range of 0.5 – 250 ppm were then used. Additionally, the gas discrimination power was tested using the standard pattern recognition algorithms Principal Component Analysis (PCA) and Linear Discrimination Analysis (LDA). Signal reproducibility was examined in an experiment exposing the microarray to five gas pulses of 10 ppm. Furthermore, the influence of changing humidity on the microarray was tested.

The studies were completed by practical tests using the KAMINA. Several materials were burnt in a furnace and the gases formed were examined. In addition to response behavior, possibilities were investigated of distinguishing between different burning materials. In another experiment, the ability was tested to differentiate between solvents and the gases of overheated wire insulation. Furthermore, the system was trained to distinguish between fire gases and diesel engine exhaust.

6. Results and Discussion

6.1 Microarray test with defined single gas exposures

Measurements of the microarray´s response to single model gas exposures showed that the SP chip was the most appropriate microarray for fire gas analysis. The optimal temperature span for chip operation turned out to be 200 – 250 °C. The following results have been achieved using SP chips.

Fig. 4 shows the resistances of all 38 elements versus the elapsed time or the median in a typical pulse exposure experiment. In this example, the gas sensor microarray was tested with pulse exposures of CO concentrations in the range of 0.5 to 250 ppm. Dur-

ing the time in between the testing gas pulses, the microarray was exposed to clean humid air of 60 % r. h., with the sensor response immediately following the rising CO concentration. The t_{90} response times were usually below 1 min. Using the KAMINA, response times of a few seconds are possible. As contrary to conventional laboratory electronics, the KAMINA has an output rate of 1 signal per second. A sensor signal for 0.5 ppm CO was produced.

The signal S is defined as the relative conductivity change with respect to the reference gas (clean humid air) $S = [Ro / R] - 1$ with Ro = reference resistance. Fig. 5 shows the median signal of all sensor elements. It can clearly be seen that the median signals of all gases (formaldehyde, benzene, tetrafluoro methane, hydrogen cyanide, carbon monoxide) are above the significance level, which is defined as triple noise level. Moreover, the comparison of the signal from the first test to that of a repeated test (one months later) only shows a slight decrease of the sensor response. This means sensor stability is reasonably good. Moreover, separate long term investigations with alcohol exposures have shown that this kind of sensitivity loss only occurs during the first 100 days after fabrication, while later sensitivity nearly remains constant (it was tested up to 400 days).

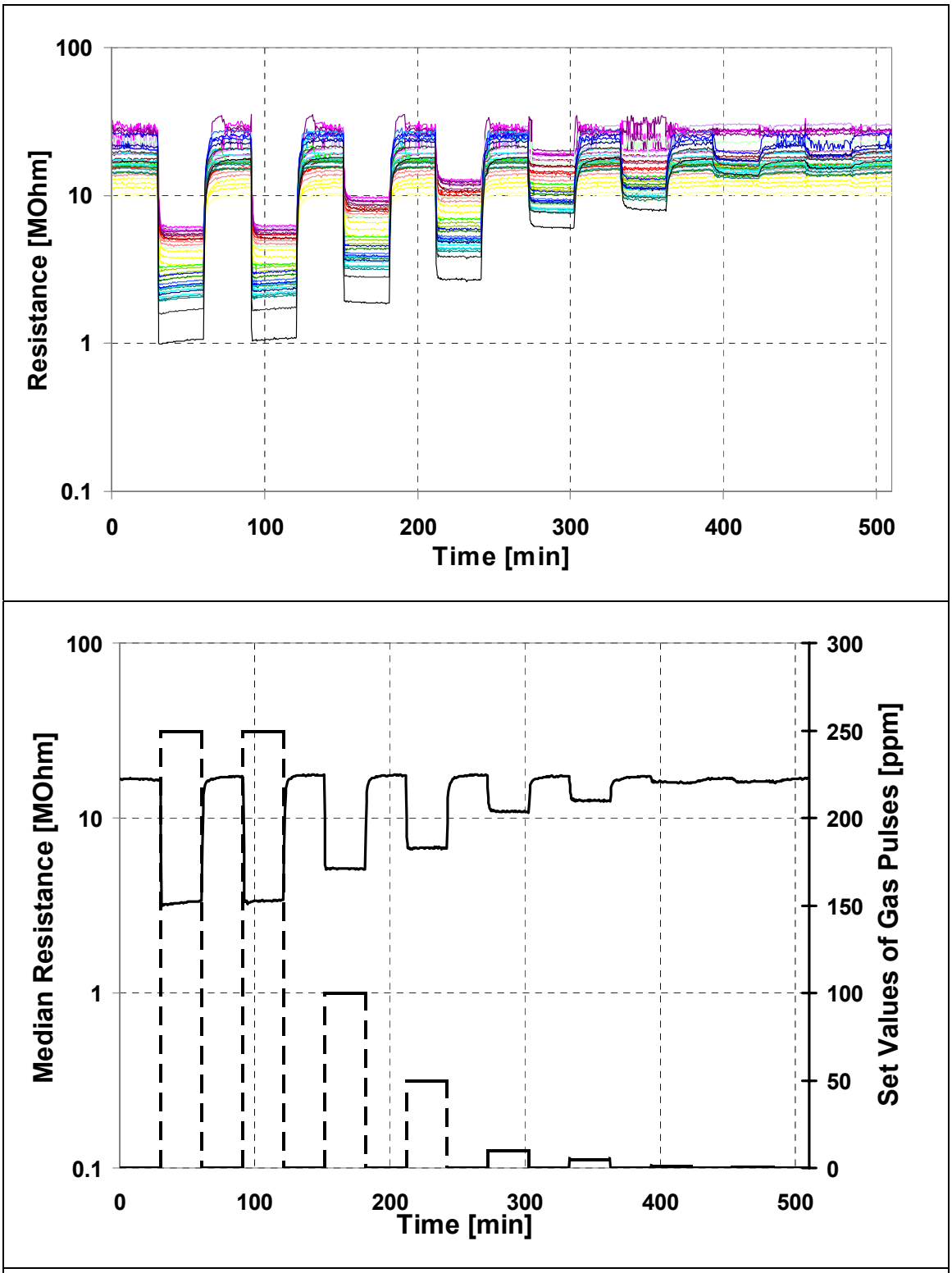


Fig. 4: Measurement of CO pulse exposures (0.5 – 250 ppm); upper plot: the resistances of all 38 sensors versus time; lower plot: the median signal and the set values of the CO concentration (broken line)

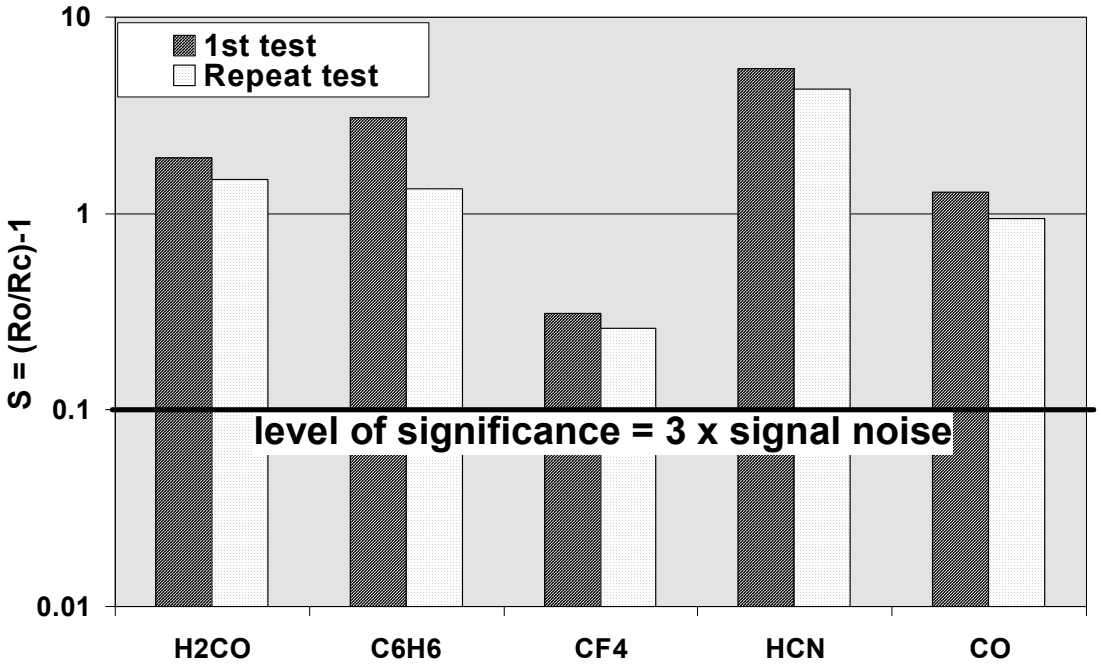


Fig. 5: Median signal of the SP chip (T = 200 – 250 °C, gas concentration 10 ppm); comparison of the 1st to a repeated test after 1 month

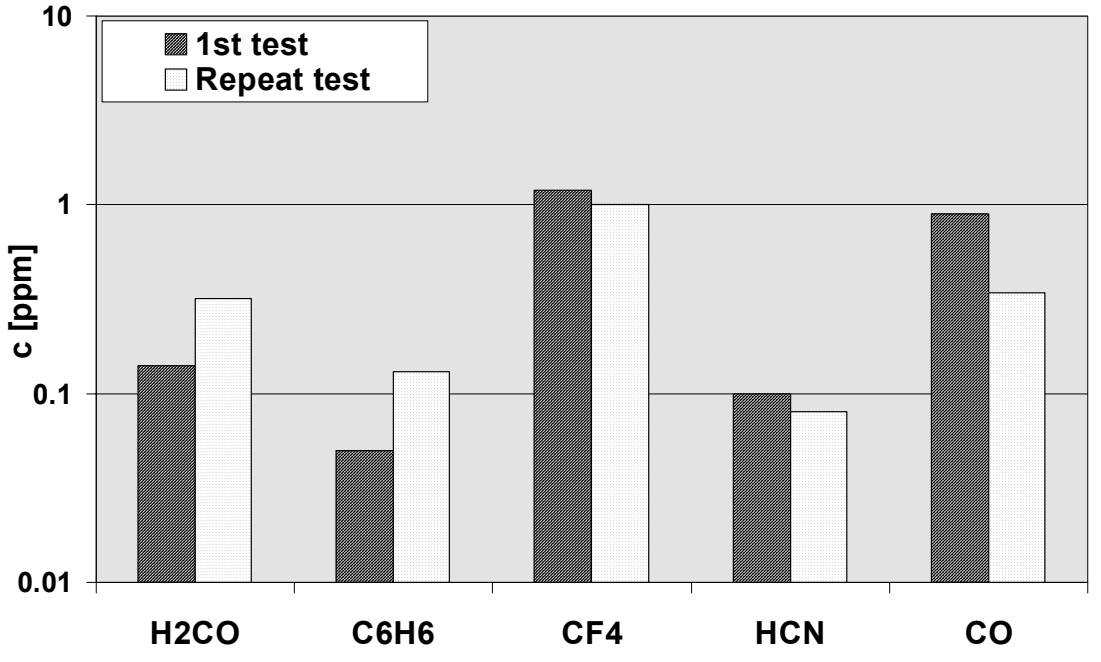


Fig. 6: Detection limits of SP chip (T = 200 – 250 °C); comparison of the 1st to the repeated test after 1 month

Furthermore, reproducibility was examined measuring sequences of five 10 ppm pulses for every gas. The mean deviation of the sensor signal was 3.6 %, at a maximum of 6 %. No cross sensitivity to humidity could be detected in the range of 40 –90 % r. h. Only a statistical scatter of the median signal with a standard deviation of 8 % was measured in the examined humidity range.

Fig. 6 shows the detection limits of the test gases. The detection limit of CF_4 was 1 ppm as CF_4 is less active and only the adsorption of the molecule established a change of the metal oxide conductivity. All other detection limits were far below 1 ppm. Especially hydrogen cyanide could be detected very easily. Repeated tests showed that the detection limits mostly remained constant: the detection limits of benzene and formaldehyde were a little higher than before, whereas the detection limits of CF_4, HCN, and CO were even slightly lower. These results again stand for good long time stability.

6.2 Distinction between different burning materials

The most important feature of an intelligent electronic nose system, as the gradient microarray, is the ability to distinguish between various kinds of gases. Therefore any difference in the composition of the gas ensemble released by different kinds of burning materials should cause the signal pattern of the microarray to respond in a characteristic way according to the burning material. Even the heat-up phase before burning should give rise to a characteristic signal pattern according to the specificity of the gas. However, the spreading of the fire changes the composition and the temperature of the burning materials which in return results in a continuous variation of the fire gases. Nevertheless, the signal inventory of the microarray obtained from real fire gases was examined in terms of its significance of discrimination of burning materials.

The signal patterns of the microarray consisting of resistances normalized “to the signal median” were examined by an LDA model. In Fig. 7 the resulting LDA diagram clearly depicts separate fields of clean air, fire gases from wool and PVC. Fire gases from wood, PE, PS and PU form a further field, which is separate from the other ones. Thus, first of all the occurrence of fire gases can be clearly distinguished from clean air and it does seem possible to make predictions about the types of burning materials with the help of the microarray. The spread of the signals within their cluster is due to the pattern

variation in the course of a burning process. In all fire experiments the microarray responded to the gases within a few seconds only.

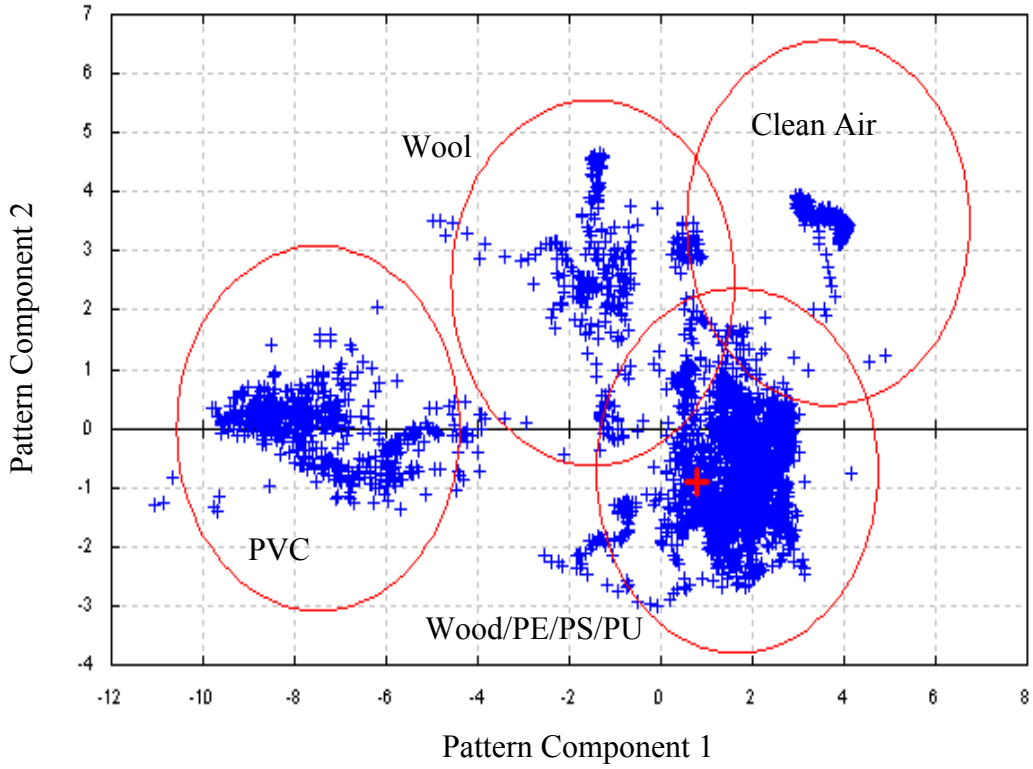


Fig. 7: LDA of the signal inventory obtained while the microarray was exposed to real fire gas. The resistances were normalized to the median signal. Discrimination between fire gases of different burning materials and clean air is attain to high extent (PE: polyethylene, PS: polystyrene, PU: polyurethane, PVC: polyvinyl chloride). A gradient microarray with 38 sensor segments based on Pt-doped SnO_2 was used for the measurement. The surface temperature of the array chip was hold at 250 – 300 °C. The area limits describe a confidence range of 95 %.

6.3 Distinction between solvents and overheated wire insulation

An important feature of a fire detector is its selectivity in terms of recognition of fire events, thus preventing false alarms caused by other sources that emit solvent vapors, such as cleaning processes. Fig. 8 shows the result of a test carried out with different kinds of overheated wire insulation as they could occur in pre-fire situations and a selection of solvents. The microarray very quickly responded to every single sample. By

using the signal pattern evaluation technique of an LDA, not only differentiating between the classes fire gases and solvents but also distinguishing between individual solvents and insulation materials became possible. Hence, a reliable detection of overheated wire insulation is feasible. However, more data has to be collected from pre-fire situations and situations in which there is no danger of fire, but similar gas components are in the air. Although the gradient microarray hardware already provides a sufficient gas discrimination power, a broad data base is necessary to design appropriate recognition of signal patterns, ensuring a reliable detection of pre-fire situations.

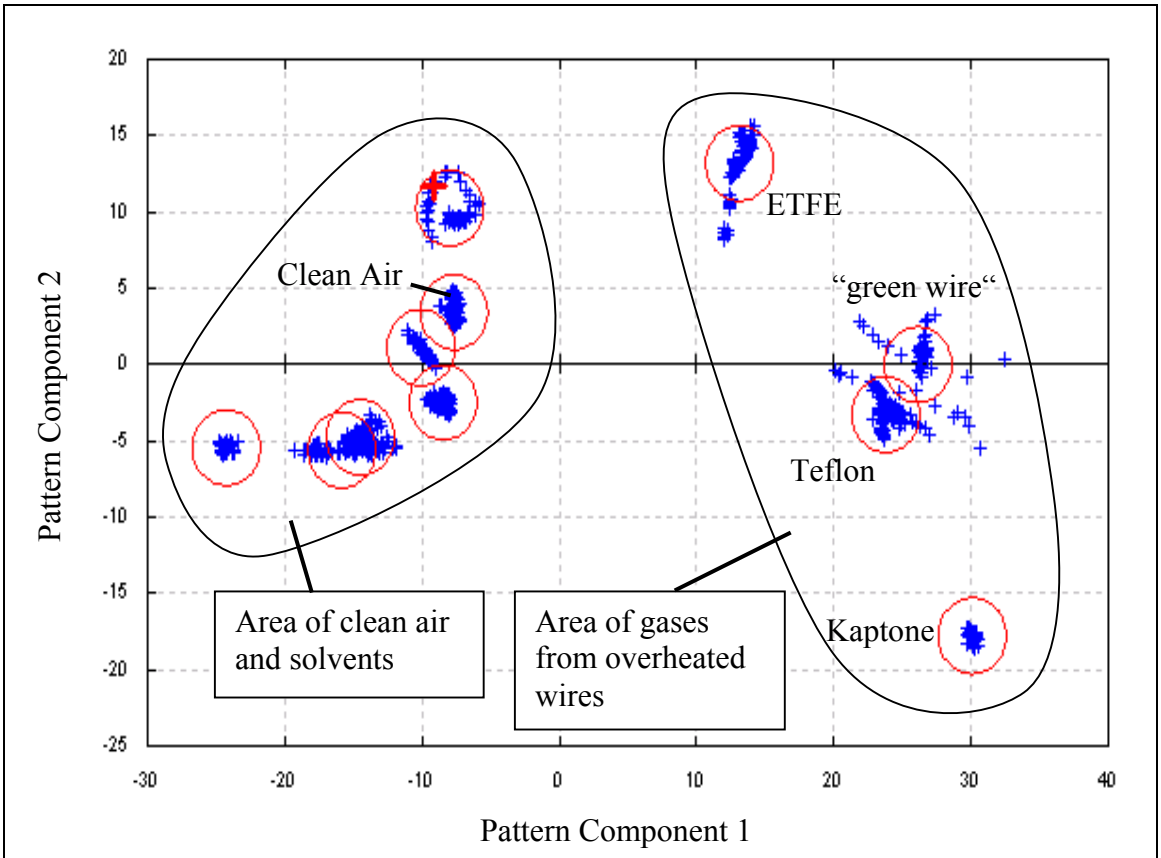
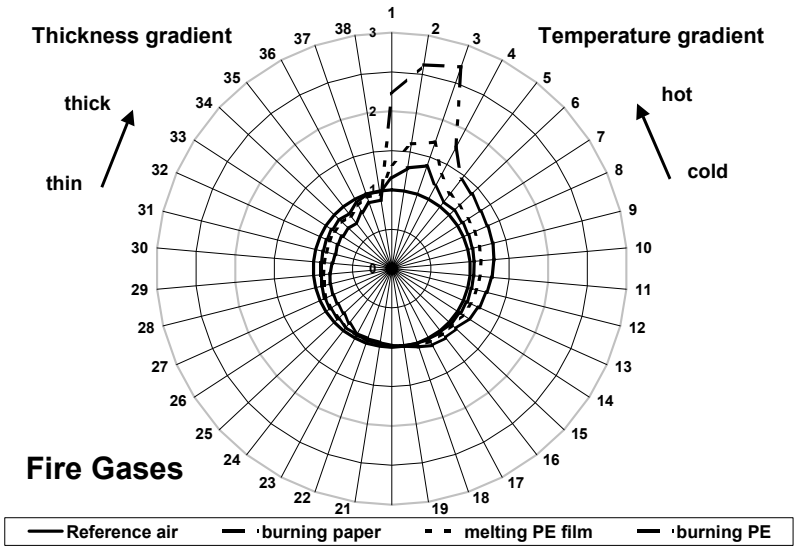


Fig. 8: Distinction between clean air, solvents and overheated wire insulation in an LDA diagram; solvents (isopropanole, ethanole, xylene, toluene, acetone, WD40) are clearly depicted separately from pre-fire gases of hot wires mantled with kaptone, fluorine-containing and unknown materials. A gradient microarray based on Pt-doped SnO_2 was used for measurement. Its temperature was kept at 250 - 300 °C. The area limits describe a confidence range of 95 %.

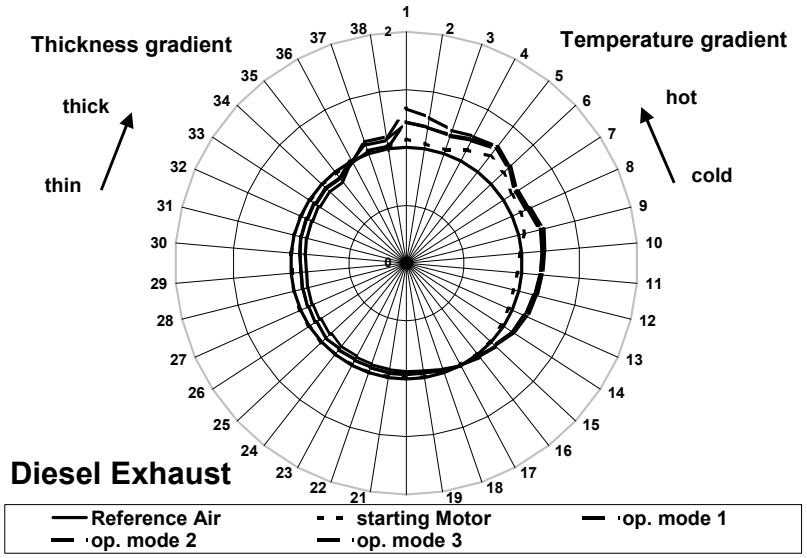
6.4 Distinction between fire gases and diesel exhaust

A deficiency of conventional fire detectors is false alarm set off by particle contaminated exhaust gases of engines, e.g. diesel engines. This problem was dealt with in another test. The following signal patterns (s. Fig. 9) were produced during measurements of the exhaust of a diesel engine and of gases from paper and polyethylene fire.

Fig. 9: Radar plots of fire gases and diesel exhaust signal patterns, normalized by the median signal.

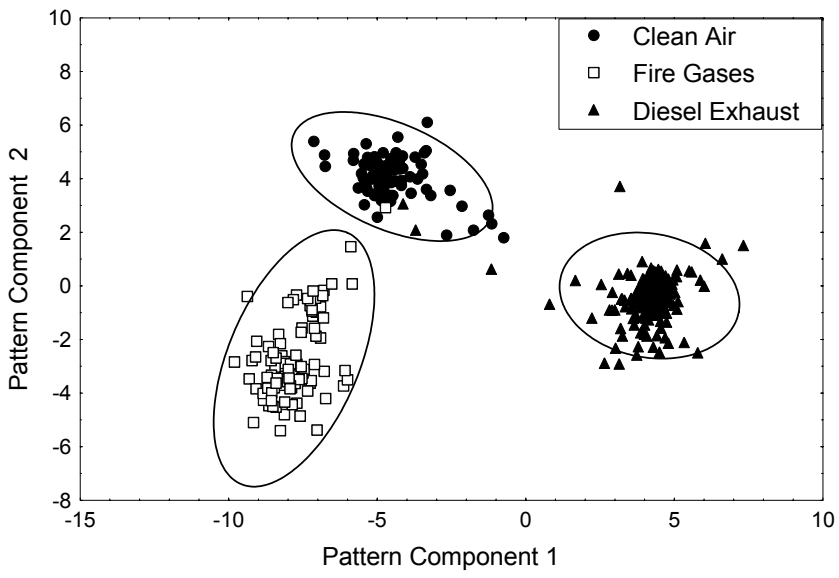


The lower plot shows the signal patterns resulting from measurements of different operation modes of the diesel engine.



From these simple radar plots the difference between the patterns can be told. Accordingly, a corresponding LDA (s. Fig. 10). shows clear separate fields representing clean air and the two gas ensembles caused by burning materials and the output of a diesel engine.

Fig. 10: Result of LDA to distinguish between fire gases and diesel exhaust based on the data of fig. 9.



7. Summary and Conclusions

Typical fire gases were sensitively detected in laboratory tests on defined conditions with a gas sensor microarray equipped with 38 sensor segments based on platinum-doped tin dioxide. The determined detection limits were 1 ppm for CF4 and far below 1 ppm for CO, hydrogen cyanide, benzene and formaldehyde. All these model gases could be clearly distinguished according to their signal patterns. Furthermore, the microarray showed very short response times within the range of a few seconds only. In several practical tests with fire gases or precursor gases of fires, the gas discrimination power of the microarray was tested, namely its signal pattern results caused by the gradient differentiation of the array´s sensor segments were checked. Possible interfering gases for the detection of pre-fire and fire gases, such as solvents or diesel exhaust, could reliably be distinguished from other true fire gases. Furthermore gas discrimination of the gradient microarray has proved to be successful for discrimination between different burning materials. Hence, the gas sensor microarray with its unique sensor element gradient differentiation offers a promising basis for development of a gas analytical fire detector.

8. References

[1] Göpel, W. and Schierbaum, K.-D., Chemical and Biochemical Sensors. in: Göpel, W., Jones, T. A., Kleitz, M., Lundström, J. and Seiyama, T., Sensors, Vol. 2, VCH, Weinheim, New York, 1991

[2] Madou, M. J. and Morrison, S. R., Chemical sensing with solid state devices. Academic Press, Inc. (London) Ltd., 1989

[3] Althainz, P., Goschnick, J., Ehrmann, S. and Ache, H. J., Multisensor microsystem for contaminants in air. Sensors and Actuators B 1996; 33: 72-76